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*Published in:*
Proceedings of the Risø International Symposium on Materials Science

*Publication date:*
2013

*Document Version*
Publisher's PDF, also known as Version of record

Proceedings of the 34th Risø International Symposium on Materials Science:
*Processing of fibre composites – challenges for maximum materials performance*
Editors: B. Madsen, H. Lilholt, Y. Kusano, S. Fæster and B. Ralph
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Technical University of Denmark, 2013

# DETERMINATION OF THE GEL POINT OF A POLYFURFURYL ALCOHOL RESIN AND CHARACTERIZATION OF ITS CURING RHEOKINETICS

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## ABSTRACT

The determination of the gel point of a resin is a key in order to design and optimize the manufacturing process of composite materials. In this work, the gel point of a biobased polyfurfuryl alcohol (FA) resin has been determined by rheological isothermal tests at different curing temperatures. The obtained gel times using three different amounts of catalyst (2, 4 and 6 % wt.) were correlated to temperature by the Macosko model; to predict the gel time at any temperature within the studied range. Furthermore, the evolution of the complex viscosity of the FA resin after its gel point has been studied as a function of the amount of catalyst and temperature. The rate of viscosity change was compared to the rate of viscosity change during the pre-gel stage, and a clear reduction was observed. Thus, the two different curing stages (pre-gel and post-gel) can be clearly identified by the rheological behavior of the resin system. The evolution of the viscosity has been modeled using widely used rheokinetic models. Finally, since rheological properties such as viscosity and complex modulus ($G^*$) are highly sensitive to the molecular weight of a polymeric system, and they can be used as indicators of the degree-of-cure of a resin, the measured complex modulus of the FA resin has been used to determine degree-of-cure profiles for FA resins with different amounts of catalyst, and at a range of temperatures.

## 1. INTRODUCTION

The preparation of composite materials to achieve both an optimization of the manufacturing process and the final properties of the composites depending on the application requires basic knowledge of the properties of the constituent materials. Thus, the study of polymers and fibers employed as matrix and reinforcements of composite materials is of great importance. In the case of thermosetting polymers, the analysis of its kinetics of curing, and the evolution of its

properties during crosslinking of the polymer, and the transitions that may occur, gelling and vitrification, are crucial.

The gel point of a resin is defined as the point at which the behavior of the resin is more similar to a solid than to a liquid, i.e. its flow behavior is changed, and it is considered that all the polymer chains are linked together forming a polymeric network. At this point, the kinetics of the curing reactions are commonly changed compared with the pre-gel stage; e.g. the curing rate is typically reduced. The gel times of a resin under different conditions (e.g. amount of catalyst and temperature) can be obtained through rheological tests. The five criteria normally used in the literature to detect the gel point by a rheological technique are: (i) the cross-over point of the elastic modulus (G') and the viscous modulus (G'') (Tung and Dynes, 1982), (ii) the point at which tan(δ) becomes independent of the frequency (Winter, 1987), (iii) the maximum of tan(δ) (Cadenato et al., 1997), (iv) the crossing point between the tangent line of the elastic modulus curve and the baseline G'=0 (Martin et al., 2000), and finally (v) the onset of decrease in the rate of growth of the viscous modulus during the polymer cure (Harran and Laudouard, 1985).

In the present work, a study of the curing process of a biobased polyfurfuryl alcohol (FA) resin was carried out using rheology as the analysis technique. The study includes determining the gel point of the resin, using the above-mentioned first two criteria, in addition to determining the gel time dependence with amount of catalyst and temperature. Furthermore, profiles of the degree-of-cure of the resin *vs.* time were obtained through a rheological variable such as the complex modulus, and the rheokinetics for the post-gel stage were determined.

## 2. EXPERIMENTAL PROCEDURE

Rheological runs were performed using an AR Rheometer 2000 (TA Instruments©) with a 25 mm diameter upper plate and a peltier lower plate. Normal force was zeroed and fixed during the tests to prevent contact loss between the sample and plates. Five isothermal curing runs of the FA resin in the three temperature ranges 65 – 85 ºC, 55 – 75 ºC and 50 – 70 ºC (using a 5 ºC increment) for 2, 4 and 6 % wt. amounts of catalyst, respectively, were carried out for 60 min. The frequencies employed were from 1 to 10 Hz (6 frequencies equally separated on a logarithm scale), and with a 0.1 % strain. For the isothermal curing runs, a 20 ºC.min$^{-1}$ heating ramp from a starting temperature of 20 ºC was programmed in order to reach the various curing temperatures. The samples were first stabilized at 20 ºC for 2 min before the heating ramp was started. All rheological measurements were performed within the linear viscosity region of the FA resin. Three replicates were used for each experimental setting.

## 3. RESULTS AND DISCUSSION

The gel point of the FA resin was obtained by applying the criterion of the cross-over point of the elastic modulus (G') and the viscous modulus (G'') at a single frequency (1Hz), and the criterion of the point at which tan(δ) becomes independent of the frequency, i.e. when the value of the tangent is equal for all the tested frequencies. An example of this is shown in Figure 1.

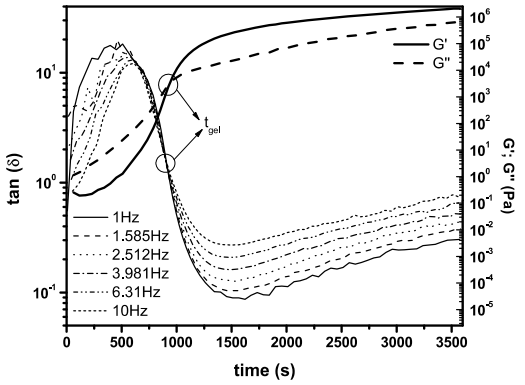


Fig. 1. Determination of gel time using the cross-over point of the elastic and storage modulus (at 1 Hz), and the point at which tan(δ) becomes independent of the frequency for a FA resin with 2 % wt. amount of catalyst and at a temperature of 75 ºC.

In the case of the second criterion, i.e. when tan(δ) becomes independent of the frequency, it was observed that at high temperatures and high amounts of catalyst, the values of gel time obtained for the three different replicates showed large variation. This second criterion was therefore rejected, and the cross-over of the moduli was taken as the most reliable criterion.

The average value of the gel time obtained for the FA resin at the tested temperatures and amounts of catalyst were determined (Table 1). The natural logarithm of the inverse of the gel times is plotted *vs.* the inverse of the absolute temperature in Figure 2.

Table 1. Gel times for FA resin for different amounts of catalyst and temperatures determined using the two criteria: cross-over of the moduli and independent value of tan(δ).

| **Amount of catalyst** | **Temperature (ºC)** | **$t_{gel}$ (s) cross-over** | **$t_{gel}$ (s) tan(δ)** |
|---|---|---|---|
| **2 % wt.** | 65 | 2544 ± 253 | 2641 ± 75 |
| | 70 | 1425 ± 8 | 1461 ± 28 |
| | 75 | 1056 ± 226 | 936 ± 21 |
| | 80 | 657 ± 44 | 666 ± 5 |
| | 85 | 448 ± 103 | 457 ± 6 |
| **4 % wt.** | 55 | 1875 ± 126 | 2004 ± 134 |
| | 60 | 1204 ± 21 | 1235 ± 27 |
| | 65 | 744 ± 18 | 754 ± 8 |
| | 70 | 452 ± 25 | 455 ± 3 |
| | 75 | 297 ± 1 | — |
| **6 % wt.** | 50 | 1579 ± 191 | — |
| | 55 | 911 ± 63 | — |
| | 60 | 555 ± 33 | — |
| | 65 | 347 ± 56 | — |
| | 70 | 230 ± 13 | — |

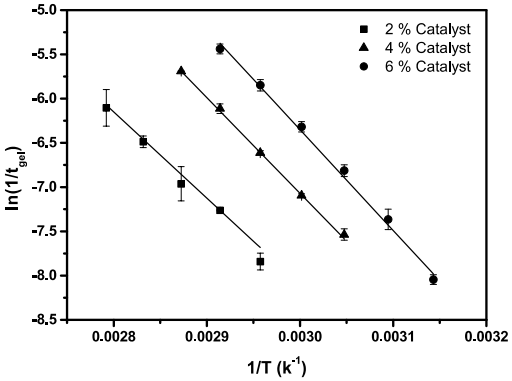


Fig. 2. Logarithm of the inverse of the gel time vs. inverse of the temperature for FA resins with the three amounts of catalyst, together with fitted model lines according to the Macosko model.

The Macosko model (Mussatti and Macosko, 1973), as described by Eq. (1), which relates the gel time to the temperature, was fitted to the results as shown in Figure 2.

$$1/t_{gel} = C \cdot \exp\left(-\Delta E_k / R \cdot T\right) \tag{1}$$

The activation energy of the process ($E_k$) together with the frequency factor (ln(C)) were obtained for the different amounts of catalyst. Both parameters consistently increased as the amount of catalyst was increased, as shown in Table 2.

Table 2. Calculated parameters of the Macosko model.

| Amount of catalyst | Ln (C) | $\Delta E_k$ (kJ.mol$^{-1}$) | $R^2$ | σ |
|---|---|---|---|---|
| **2 % wt.** | 21.1 ± 2.1 | 81.0 ± 5.9 | 0.984 | 1.058 |
| **4 % wt.** | 25.4 ± 0.2 | 90.0 ± 0.5 | 1.000 | 0.549 |
| **6 % wt.** | 27.8 ± 1.1 | 94.8 ± 2.9 | 0.995 | 1.133 |

In the case of the determined values of the activation energy, there is a clear difference when using the low 2 % wt. amount of catalyst ($\Delta E_k$ = 81 kJ.mol$^{-1}$) compared to the higher 4 and 6 % wt. amounts of catalyst ($\Delta E_k$ about 92 kJ.mol$^{-1}$). This same tendency was also found for the curing activation energies obtained by DSC by the Belichmeier method – also a single point method – in previous work by the authors (Domínguez and Madsen, 2011). The smaller difference found between 4 and 6 % wt. amounts of catalyst suggests that a maximum of the curing rate is approached. Altogether, as demonstrated by the quality of the fits shown in Figure 2, it is proven that the Macosko model is quite suitable to be used to predict the gel time of the FA resin at the temperatures commonly used in the manufacturing of FA resin composite materials (Domínguez and Madsen, 2013).

Once the dependence of the gel point of the FA resin on temperature for each of the used amounts of catalyst was determined, the evolution of the degree-of-cure during the post-gel stage was estimated by monitoring a rheological variable such as the complex modulus ($G^*$) using Equation (2).

$$\alpha(t) = \frac{\log(G^*(t)) - \log(G^*(t_{\alpha=0}))}{\log(G^*(t_{\alpha=1})) - \log(G^*(t_{\alpha=0}))} \quad (2)$$

This model is one of the different models proposed in the literature for the estimation of the degree-of-cure (Domínguez et al., 2010). The degree-of-cure is related to the increase in the logarithm of the complex modulus throughout the curing process, i.e. from the modulus measured for the uncured resin to the modulus measured for the fully cured resin. In the present study, if the FA resin was not fully cured at the end of the test, the complex modulus of the fully cured resin was estimated by Eq. (2) using the determined complex modulus at the gel-point ($G^*(t_{gel})$) and the previously determined degree-of-cure at the gel point ($\alpha(t_{gel})$) on 0.50 for the FA resin (Domínguez et al., 2012; Guigo et al., 2007). The complex modulus used to calculate the obtained degree-of-cure of the FA resin corresponds to a frequency of 1 Hz, which is the same frequency employed in the gel point determination. The evolution of the degree-of-cure of the FA resin is shown in Figure 3 for the three amounts of catalyst, and at a temperature of 65 ºC.

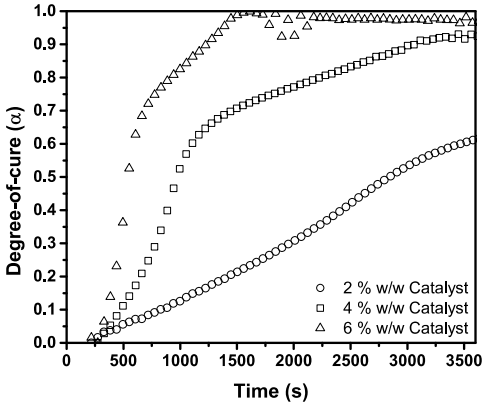


Fig. 3. Evolution of the degree-of cure of the FA resin at 65 ºC.

The degree-of-cure of the FA resin reached at the end of the performed experiments, i.e. after an hour of curing (3600 seconds, see Figure 3) under isothermal conditions, for each of the temperatures and amounts of catalyst is shown in Table 3. For those trials in which the resin has been fully cured, the average time required to reach final cure has also been determined.

Table 3. Reached degree-of-cure of the FA resin at different temperatures and amounts of catalyst.

| Temperature [ºC] | Amounts of catalysts | | |
|---|---|---|---|
| | 2 % wt. | 4 % wt. | 6 % wt. |
| 50 | — | — | 0.727 ± 0.020 |
| 55 | — | 0.710 ± 0.018 | 1.000 (3382 ± 160)* |
| 60 | — | 0.832 ± 0.010 | 1.000 (2238 ± 168)* |
| 65 | 0.661 ± 0.035 | 0.908 ± 0.030 | 1.000 (1478 ± 142)* |
| 70 | 0.809 ± 0.068 | 1.000 (2243 ± 4)* | 1.000 (950 ± 122)* |
| 75 | 0.862 ± 0.012 | 1.000 (1586 ± 1)* | — |
| 80 | 0.882 ± 0.023 | — | — |
| 85 | 0.972 ± 0.050 | — | — |

* Time (s) required to fully cure the FA resin.

All the obtained degree-of-cure profiles of the FA resin, as exemplified in Figure 3, show a marked change in the slope at a given time interval, and this is due to a change in the kinetics of the curing process. This change occurs once the FA resin exceeds the degree-of-cure at the gel point, which is determined in previous studies to be approximately 0.50 (Domínguez et al., 2012; Guigo et al., 2007), and this is in good agreement with the results shown in Figure 3. The observed reduction of the curing rate after the gel point is in agreement with previously results showing a tendency for the activation energy to be reduced in the proximity of the gel point (Domínguez et al., 2012). Thus, it is shown that in the case of FA resins, the study of curing kinetics must be split in two stages, pre-gel and post-gel, applying for each stage the most suitable models for the determination of the curing kinetic parameters.

The cure kinetics models applied to the complex viscosity measured beyond the gel point of the FA resin are the four- and six-parameter Arrhenius models, which are described by Equations (3) and (4), respectively:

$$\mathrm{Ln}\left(\eta^{*}\left(t\right)\right)=\mathrm{Ln}\left(\eta_{\infty}^{*}\right)+\frac{\Delta E_{\eta}}{R\cdot T}+t\cdot k_{\infty}\cdot\exp\left(\frac{-\Delta E_{k}}{R\cdot T}\right) \tag{3}$$

$$\mathrm{Ln}\left(\eta^{*}\left(t,T\right)\right)=\mathrm{Ln}\left(\eta_{\infty}^{*}\right)+\frac{\Delta E_{\eta}}{R\cdot T}+\frac{\phi}{n-1}\cdot\mathrm{Ln}\left(1+\left(n-1\right)\cdot t\cdot k_{\infty}\cdot\exp\left(\frac{-\Delta E_{k}}{R\cdot T}\right)\right) \tag{4}$$

where $\eta^{*}$ is the complex viscosity at absolute temperature T, $\eta^{*}_{\infty}$ is the reference viscosity at "infinite temperature", $\Delta E_{\eta}$ is the Arrhenius activation energy for viscosity, t is the curing time, R is the universal gas constant, $k_{\infty}$ is the kinetic constant analogue of $\eta^{*}_{\infty}$, and $\Delta E_{k}$ is the kinetic activation energy analogue to $\Delta E_{\eta}$, $\varphi$ is a proportionality factor ($\varphi$) and n is the reaction order.

The curing parameters of the FA resin for its post-gel stage were calculated by applying a minimization algorithm of residual sum of squares (RSS) using Matlab. The obtained results for the Arrhenius four- and six-parameter models are shown in Table 4, together with the calculated total error (including all three replicates) of the model for all the temperatures tested.

Table 4. Determined values for the parameters of the four and six-parameter Arrhenius models.

| Model | Catalyst | $-\Delta E_k$ (kJ/mol) | $\mathrm{Ln}(k_\infty)$ | $\phi$ | n | MSE* |
|---|---|---|---|---|---|---|
| **Arrhenius 4p.** | 2 % | — | — | — | — | — |
| | 4 % | 62.1 | 16.51 | — | — | 0.898 |
| | 6 % | 58.9 | 15.95 | — | — | 0.695 |
| **Arrhenius 6p.** | 2 % | 104.4 | 32.79 | 0.62 | 1.40 | 0.897 |
| | 4 % | 79.9 | 23.96 | 0.88 | 1.27 | 0.180 |
| | 6 % | 60.5 | 17.23 | 0.92 | 1.17 | 0.136 |

*Mean Square Error.

As expected, the Arrhenius four-parameter model cannot predict correctly the behavior of the complex viscosity of the FA resin since this model is only valid for linear increasing viscosity behavior. This is revealed by the high total error evaluated through the MSE values calculated for the 4 and 6 % wt. amounts of catalyst. In the case of the 2 % wt. amount of catalyst, the model was applied to the data but the curing parameters provided by the model were meaningless, and they are therefore not shown in Table 4. A clearly curved evolution of the

logarithm of the complex viscosity of the FA resin was found, as exhibited in Figure 4, and therefore a more sophisticated version of the Arrhenius model was required to obtain suitable predictions, namely the Arrhenius six-parameter model.

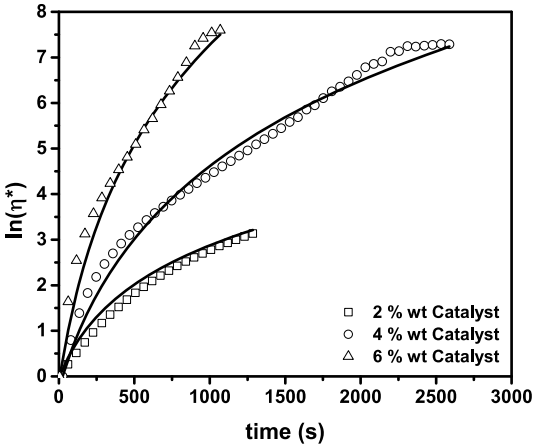


Fig. 4. Post-gel evolution of the logarithm of the complex viscosity of the FA resin at 65ºC. Experimental data (symbols) and model predictions by the Arrhenius six-parameter model (lines).

The Arrhenius six-parameter model can predict the behavior of the complex viscosity of the FA resin during the post-gel curing stage quite correctly, as shown in Figure 4. In particularly, good predictions are found for the 4 and 6 % wt. amounts of catalyst as shown by the low MSE values (Table 4). In contrast, the MSE value for the 2 % wt. amount of catalyst is higher, and close to the values obtained for the four-parameter model. This is expectedly due to the scattered values of the complex viscosity found for high temperatures (80-85 ºC) when a 2 % wt. amount of catalyst was used. These scattered values can be explained by the possible small gradients of the catalyst in the resin (i.e. non-perfect mixing), and the effect of these gradients becomes more significant at high temperatures, and thereby at high curing rates.

## 4. CONCLUSIONS

The following conclusions can be extracted from the present study:

- The gel time of a FA resin with different amounts of catalyst was measured at different temperatures by a rheological technique. The Macosko model was successfully applied to the experimental data. The model allows predicting gel times of the FA resin when using any of the tested amounts of catalyst, and within the range of the tested temperatures.

- The evolution of the degree-of-cure of the FA resin was estimated under isothermal conditions by a rheological analysis of its curing process, and by monitoring only rheological variables. Two curing stages were found, and they were clearly marked by the gelation of the resin, i.e. pre- and post-gel stages. This confirms the results found in a previous study of the curing process of the FA resin.

- The rheokinetic parameters of the FA resin curing process were calculated for two of the

three amounts of catalyst used, 4 and 6 % wt., by the Arrhenius six-parameter model, which was found to be the most suitable model. The modeling of the curing process when a 2 % wt. catalyst was used could not be conducted satisfactorily.

## ACKNOWLEDGEMENTS

The authors are grateful for the support from "Ministerio de Educación" (Spanish Government) for financial support (Programa Nacional de Movilidad de Recursos Humanos del Plan Nacional de I-D+i 2008-2011). The research has been funded by the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement nº 210037 (WOODY).

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